# Hydrogen Storage in Carbon-based Materials

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*This presentation contains no proprietary information*

# Objective

- Advance performance of on-board adsorbents in support of DOE Multi-year Program Plan.

- Demonstrate accuracy of hydrogen measurements on adsorbent materials.

- Develop methods to reproducibly activate and handle materials to permit scale-up and validation of hydrogen uptake.

- Widen scope and throughput to develop scientific and technical basis for adsorbent use in hydrogen storage.

100 Å
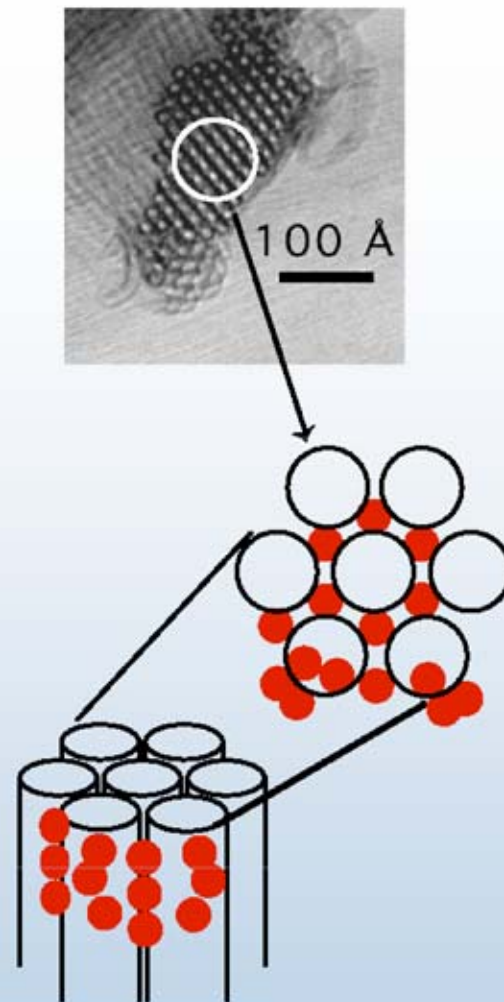
DOE 2010 Technical Targets for Storage System
- Gravimetric    0.06 kg $H_2$/ kg system
- Volumetric     0.045 kg $H_2$/ kg

# Budget

**Budget/Actual Spending ($k)**

| | Qtr 1 | | Qtr 2 | | Qtr 3 | | Qtr 4 | | YTD Total | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Plan | Actual | Plan | Actual | Plan | Actual | Plan | Actual | Plan | Actual |
| NREL | 268 | 291 | 386 | 361 | 391 | 0 | 473 | 0 | 654 | 652 |
| Subcontractors | 0 | 0 | 8 | 2 | 62 | 0 | 63 | 0 | 8 | 2 |
| Total | 268 | 291 | 394 | 363 | 453 | 0 | 536 | 0 | 662 | 654 |

- Subcontract funds support:
    - Prof. T. Gennett on two-year sabbatical at NREL from RIT
    - T. McDonald, graduate student from Columbia U., performing PhD Thesis work at NREL
- Total FY04 budget: $2 M

# On-Board Hydrogen Storage Barriers & Targets

**General:**
- A. Cost.
- B. Weight and Volume.
- C. Efficiency.
- E. Refueling Time

**Reversible Solid-State Material**
- M. Hydrogen Capacity and Reversibility.
- N. Lack of Understanding of H Physi- and Chemisorption.
- O. Test Protocols and Evaluation Facilities.

**Crosscutting Relevance**

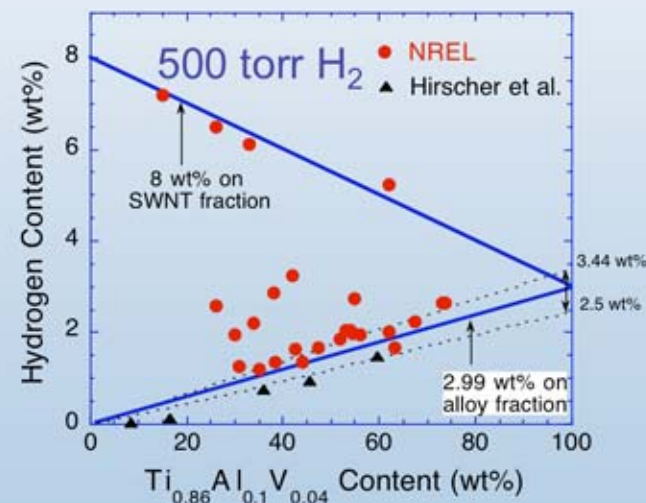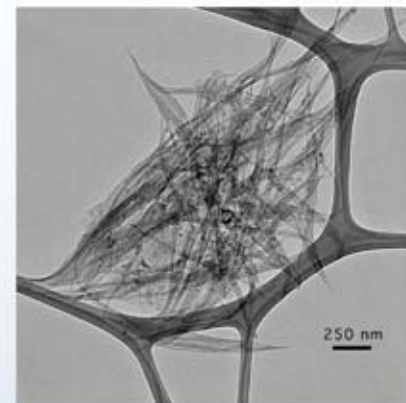Compressed Gas Systems Barrier H:
Sufficient Fuel Storage for Acceptable Vehicle Range.

Off-Board Hydrogen Storage Barriers S & T:
Cost and Efficiency

# Approach

- **Develop carbon-based materials for high volumetric and gravimetric hydrogen storage**

  - Reproducibility
    - In-house review of measurement techniques
    - Repeatable methods to prepare high-capacity samples
    - Validation in external lab

  - Understand physics/chemistry of adsorption
    - Discern mechanisms with computational methods
    - Experimentally probe mechanisms
    - Broaden investigation beyond carbon nanotubes
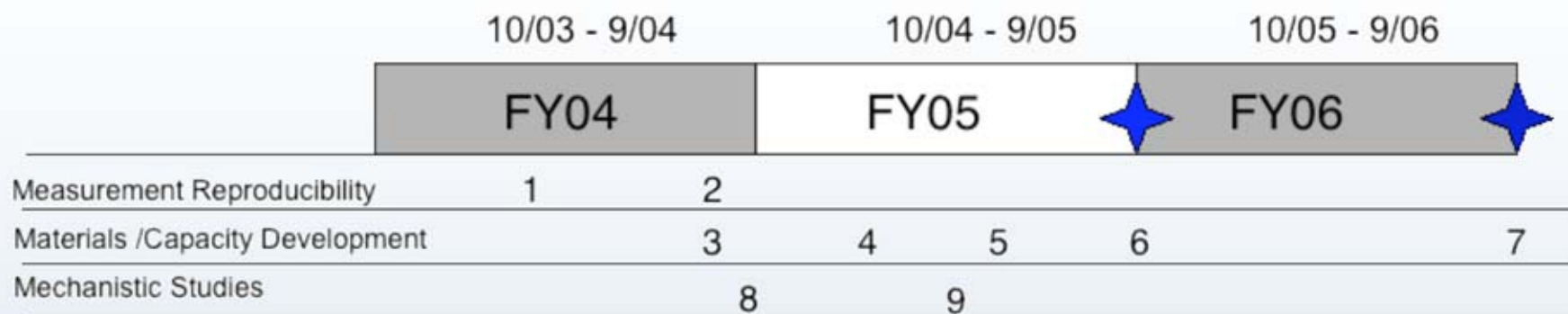
  - Engineer and fabricate best $H_2$ adsorbent



250 nm



500 torr $H_2$   ● NREL   ▲ Hirscher et al.

Hydrogen Content (wt%)

8 wt% on SWNT fraction

3.44 wt%
2.5 wt%
2.99 wt% on alloy fraction

$Ti_{0.86}Al_{0.1}V_{0.04}$ Content (wt%)

Heben, M.J., et al. AIP, Vol. CP671, 77 (2003)

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# Project Safety

- Adsorbents under investigation are not pyrophoric or highly flammable.

- In application, adsorbents will operate at lower pressures (< 100 bar) than compressed gas storage (680 bar), thereby reducing physical hazards.

- NREL uses rigorous safety controls for $H_2$, applying experience gained from handling flammable, toxic, and pyrophoric gasses for solar cell research.

- Liquid-suspended nanotubes and other nanoparticles have shown some potential for toxicity[1]. Proper handling in the lab avoids these concerns, and these issues should not be of great importance in application.

[1] R.F. Service, *Science* **300**, 243 (2003)

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# Project Timeline

| | 10/03 - 9/04 | 10/04 - 9/05 | 10/05 - 9/06 |
|---|---|---|---|
| | FY04 | FY05 | FY06 |
| Measurement Reproducibility | 1      2 | | |
| Materials /Capacity Development | 3 | 4      5      6 | 7 |
| Mechanistic Studies | 8 | 9 | |

**Measurement Reproducibility**
- 1 - In-house review of measurement techniques
- 2 - Agreement with measurements at external lab

**Reproducible Capacity**
- 3 - 3 wt% at room temperature
- 4 - 3 wt% verified externally
- 5 - Assess low-T, High-P capabilities
- 6 - 4 wt% at room temperature (verified externally)
- 7 - 6 wt% at room temperature (verified externally)

**Mechanistic Studies**
- 8 - Develop working theoretical model
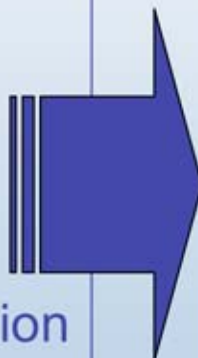- 9 - Identify most promising materials / mechanisms

# Review of Measurement Accuracy

*Tech Team Recommendation*
Performed week of 1/19 to 1/23/04 by Dr. M. Miller (SwRI) and
Prof. R. Gorte (U. Penn), with Dr. S. Satyapal (DOE) in attendance.

Pre-Review Concerns

- Use of TPD

- Potential contamination

- Calibration

- Alloy fraction determination

- Data reduction methods

Approach to Resolve Issues

- Use volumetric to confirm TPD

- Employ mass spectroscopy - use $D_2$ and $H_2$
- Blind analysis of $TiH_2$ standards

- Specify & demonstrate alloy fraction analysis
- Establish accuracy of each step, apply error analysis

# Equipment Accuracy
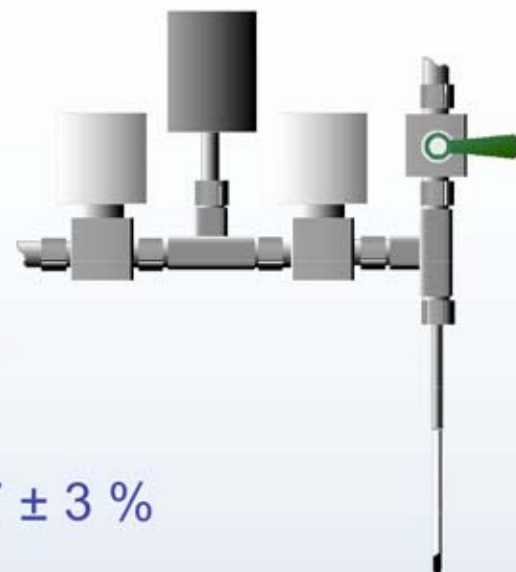
**Excellent agreement between TPD and volumetric measurements for probe metal alloy**

| TPD | 2.40 wt% |
| Volumetric | 2.49 (adsorption) |
| | 2.54 (desorption) |

→ 2.47 ± 3 %

**Excellent accuracy in blind analysis of samples**

- Systems calibrated by primary methods
- $H_2$ recovered from unknown weight of $TiH_2$ standard
- Weight determined from known H/M ratio for $TiH_2$

$H_2$ / Temperature
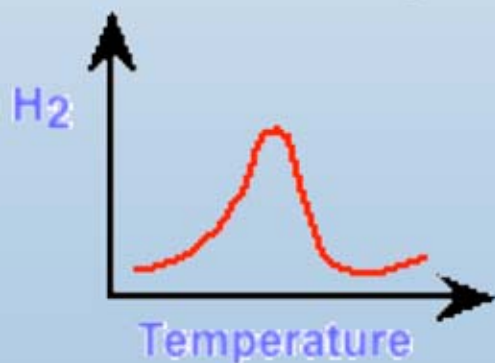
| | | Measured | Unknown | Difference |
|---|---|---|---|---|
| Vol. | | 11.11 mg | 11.40 mg | -2.57% |
| | | 5.48 mg | 5.55 mg | -1.46% |
| TPD | | 1.56 mg | 1.54 mg | 1.3% |
| | | 1.76 mg | 1.73 mg | 1.73% |

# Preparation of metal-doped SWNTs

**Step 1: laser generation of SWNTs**

produces a synthesis batch

laser

Co:Ni:C target

**Step 2: purification of SWNTs**

Reflux in $HNO_3$, collect on filter, oxidize in air
produces a purification batch (e.g. pure #1)

**Step 3: Ultrasonic cutting**

produces a "cut" batch, introduces metal
(e.g. cut #1)

**Step 4: Collect by filtration**

Bucky paper

pure #1, cut #1, piece #1

pure #1, cut #1, piece #2

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# Data Reduction: wt% H on SWNTs

(1): $X_{alloy} + X_{SWNT} = 1$

where $X_{alloy}$ and $X_{SWNT}$ are weight fractions

(2) $(wt\% \, H_{SWNT} * X_{SWNT}) + (wt\% \, H_{alloy} * X_{alloy}) = wt\% \, H_{sample}$

$$wt\% \, H_{SWNT} = \frac{wt\% \, H_{sample} - (X_{alloy} * wt\% \, H_{alloy})}{(1 - X_{alloy})}$$

Requires accurate measurement of:
- ✓ Weight of sample
- ✓ Total amount of hydrogen adsorbed
- ✓ Weight of alloy in sample
- ✓ Hydrogen capacity of alloy

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# Data Obtained During Review

| Sample | Technique | Wt% $H_2$ total | Wt% alloy | Wt% $H_2$ tubes |
|---|---|---|---|---|
| Pure #1, cut #1, piece #1 | TPD | 2.62 | 68.0 | 2.88 |
| Pure #1, cut #1, piece #2 | TPD | 2.39 | 66.4 | 2.17 |
| Pure #1, cut #1, piece #3 | Vol (abs) | 1.93 | 63.9 | 0.92 |
| Pure #1, cut #1, piece #3 | Vol (des) | 2.13 | 63.9 | 1.48 |
| Pure #1, cut #2, piece #1 | TPD | 1.90 | 41.0 | 1.48 |
| | | | | |
| Pure #2, cut #1, piece #1 | TPD | 1.09 | 22.4 | 0.68 |
| Pure #2, cut #2, piece #1 | Vol (abs) | 1.51 | 45.8 | 0.67 |
| Pure #2, cut #2, piece #1 | Vol (des) | 1.50 | 45.8 | 0.65 |
| Pure #2, cut #2, piece #2 | TPD | 1.18 | 40.4 | 0.29 |
| | | | | |
| Pure #3, cut #1, piece #1 | TPD | 1.06 | 43.3 | -0.04 |
| Pure #3, cut #1, piece #2 | Vol (abs) | 0.87 | 35.7 | 0.00 |
| Pure #3, cut #1, piece #2 | Vol (des) | 1.19 | 35.7 | 0.46 |

- Reasonable agreement between TPD and volumetric
- Differences due to degas methods, not accuracy
- Data in red show SWNT uptake after uncertainty analysis

# Uncertainty Analysis
## *Tech Team Recommendation*
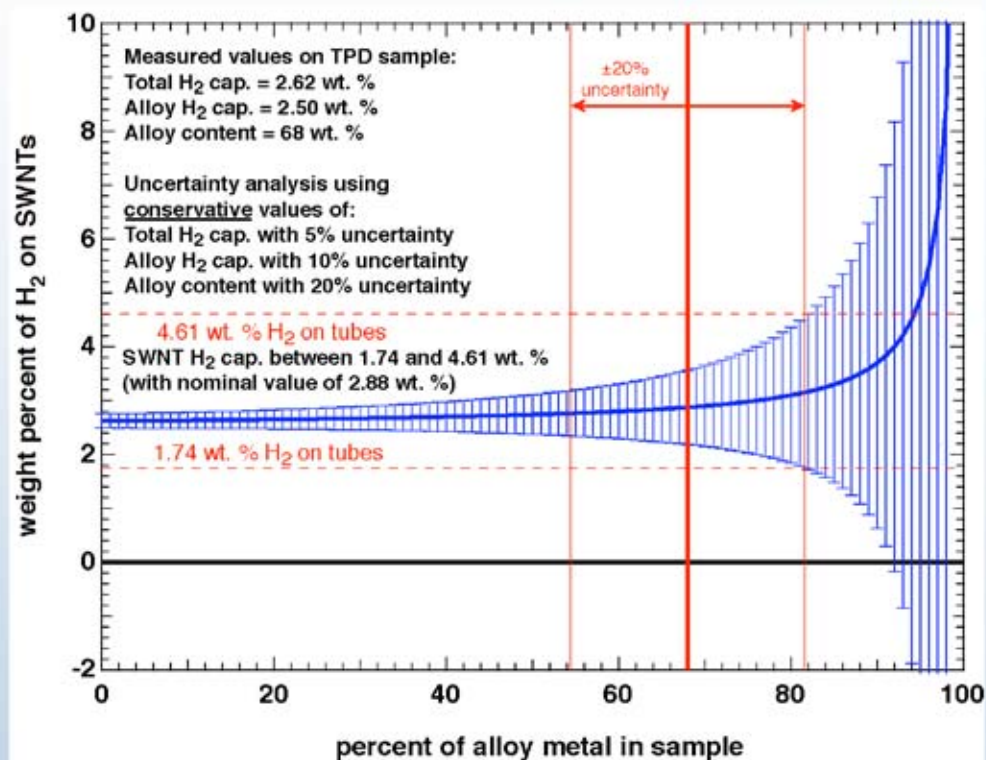


Conservative estimate of possible errors

- Analysis shows significant SWNT uptake on 2 of 9 samples
- Lower metal contents desired for less uncertainty, and higher overall gravimetric performance

# Conclusions from External Review

- $H_2$ uptake values for alloyed SWNTs as reported by the NREL team during peer review are credible
- Analytical methodologies are well established
- TPD and volumetric techniques were demonstrated to be accurate and repeatable based on reference standard
- Excellent correlation between techniques using similar samples
- Large variances in $H_2$ uptake for SWNT materials not related to analytical methodologies
  - Likely attributed to the stochastic nature of sample processing (synthesis, purification, cutting, dopant uptake)
  - Sensitivity of samples to degradation during degas cycle
- Next steps: Demonstrate 4 wt% capacity

The in-house review met a critical Jan. 04 milestone on time.

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# Towards Reproducible Activation

- Use surfactants to prepare fully solubilized, cut SWNTs

- Incorporate metal particles via sonication, or use solubilized SWNTs as precursors for more controlled carbon/metal hybrid syntheses

- Tube diameters and chiralities measured by luminescence, allowing structure and function to be linked
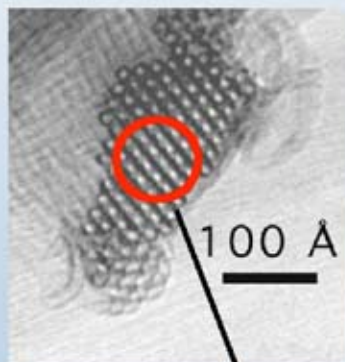
First results with SDS and high-power sonication show 3 wt% on a total sample weight basis, and 3.6 wt% on tube fraction.

100 Å

SDS

sonication
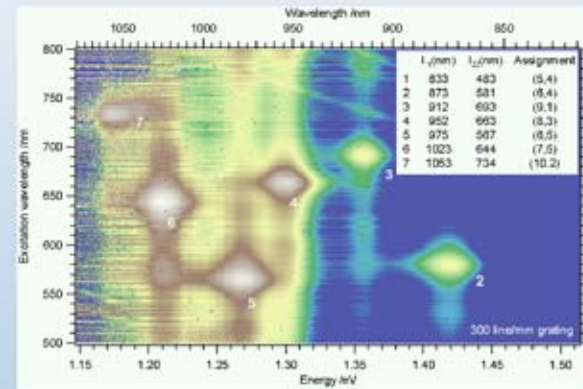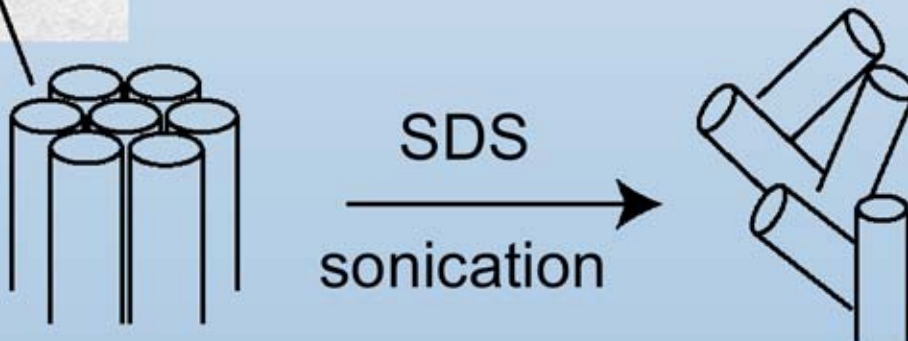
After Bachilo, et al. *Science* **298** (2002), 2361. Acknowledgements to M. Jones, C. Engtrakul, and G. Rumbles at NREL.

# Low-T, Low-pressure Adsorption

- SWNTs, MOFs, graphite fibers are more effective than activated carbons available in the 1980s and 1990s

- $E_B$ of 10 - 20 kJ/mol would permit high-density storage at cold temperatures and P < 100 bar.

- Lower pressure operation would permit the use of conformal tankage

- Early results: $CO_2$ treated raw SWNTs 0.8 wt% $H_2$ at 510 torr and 77 K

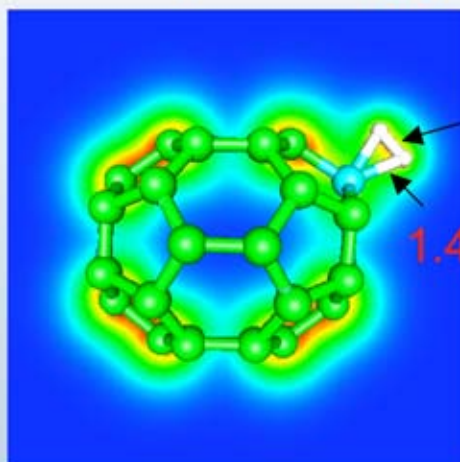- Other materials, generated internally and from collaborators, are now under investigation
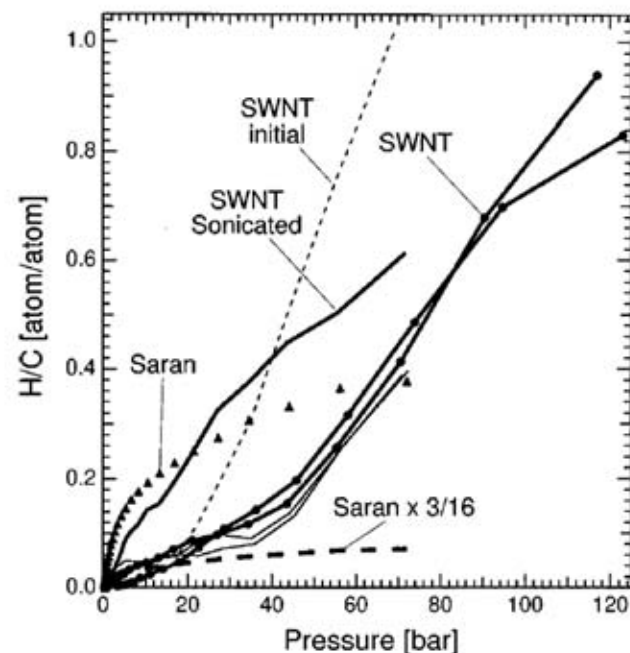


8 wt% storage on SWNTs at 80K
Ye, et al., APL 74, 2307 (1999)

# Application of Computational Chemistry

- Search for intermediate binding (10 - 50 kJ/mol) between $H_2$ physisorption (~ 4 kJ/mol) and C-H bond (~400 kJ/mol)
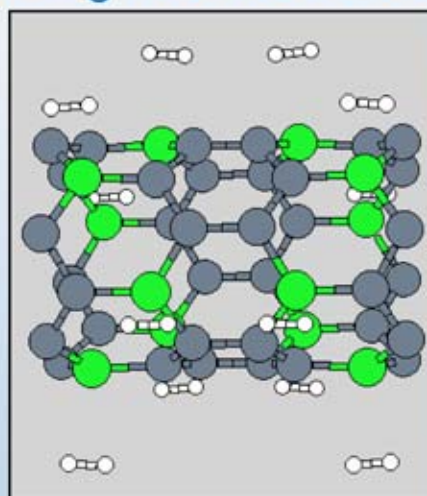
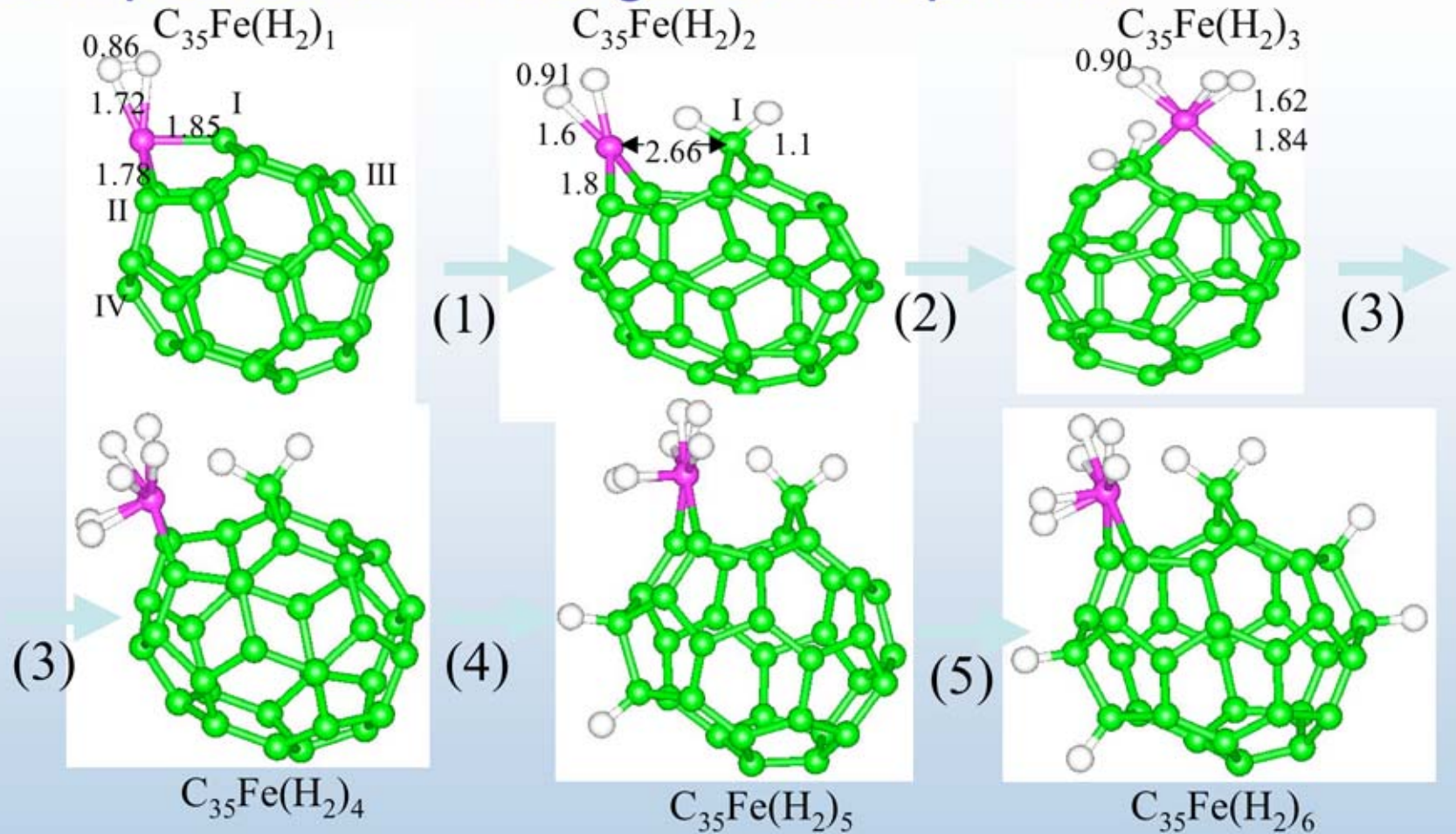### B-doped $C_{36}$

### $BC_3$ nanotubes

37 kJ/mol

0.85 Å

1.40 Å

12 kJ/mol
~ 4.2 wt%



- 3-center, 2-electron binding between $H_2$ and adsorbents
- Manipulation of binding by doping, charging & curvature
- $H_2$ bond lengthened vs. free $H_2$ (0.75 Å)
- Binding between physi- and chemisorption

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# Computational Investigation of Spillover



$C_{35}Fe(H_2)_1$ $C_{35}Fe(H_2)_2$ $C_{35}Fe(H_2)_3$

$C_{35}Fe(H_2)_4$ $C_{35}Fe(H_2)_5$ $C_{35}Fe(H_2)_6$

$H_2$ molecules first adsorb on Fe only. After three pairs, $H_2$ starts to dissociate and chemisorb on distant carbon as well, which was not possible without the substitutional Fe.  Binding Energy to Fe is ~ 50 kJ/mol but C-H binding energy is ~170 kJ /mol.
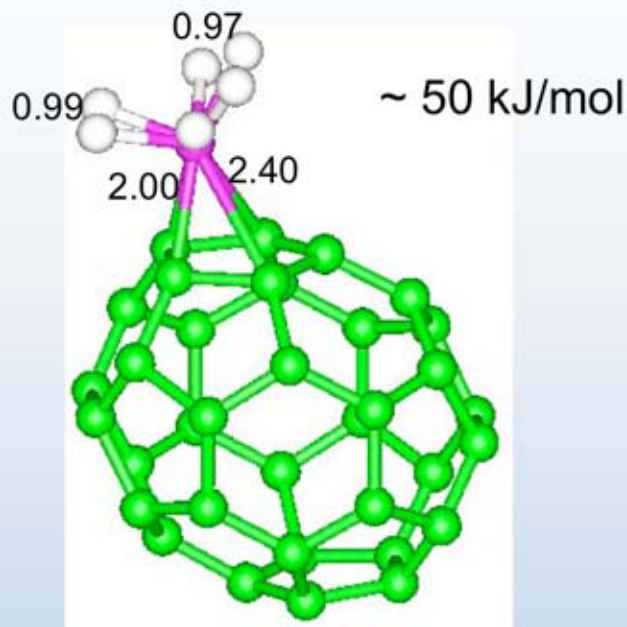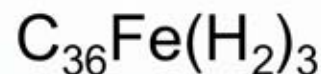
*Bond-distances are in Angstroms

# Effect of Fe Adatom on Hydrogen Adsorption on $C_{36}$

$C_{36}(H_2)_1$

$C_{36}Fe(H_2)_3$



0.75
2.52

0.97
0.99
~ 50 kJ/mol
2.00   2.40
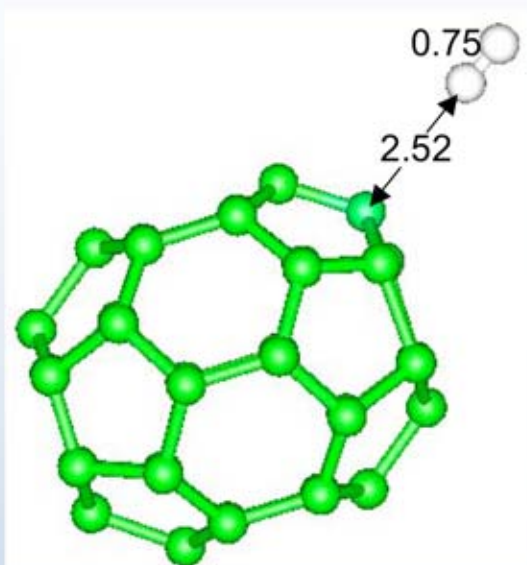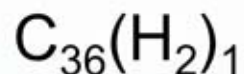
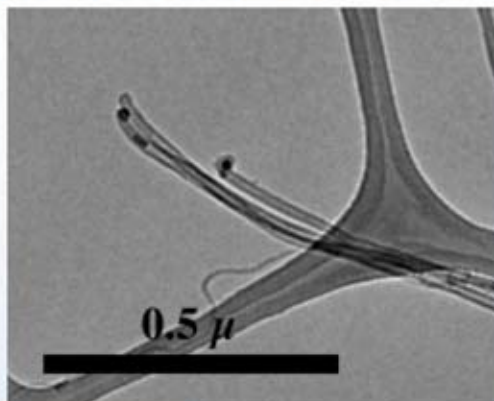$H_2$ on pure $C_{36}$: only weak physisorbtion (~ 4 kJ/mol)
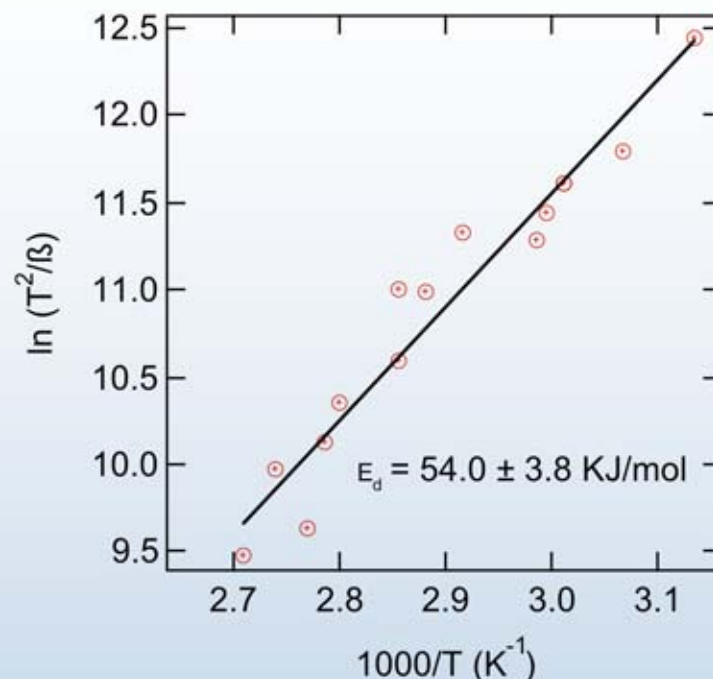
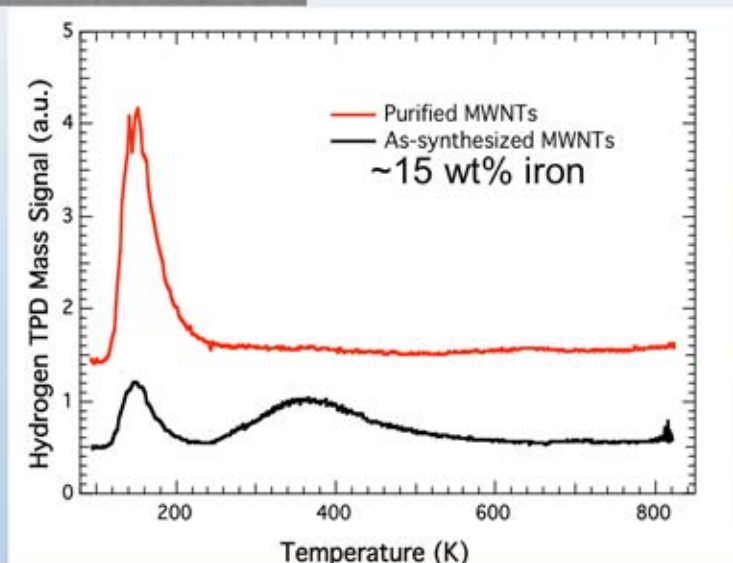*Bond-lengths are in Angstroms

Fe adatom can complex with $H_2$, but does not result in hydrogen chemi- or physi-sorption on the carbon.

Similar to Kubas Complexes:  G.J Kubas, J. Organo-metallic Chem. 635 (2001) 37-68.

# Hydrogen Storage in MWNT Materials



As-synthesized MWNTs have iron nanoparticles at tips



$E_d = 54.0 \pm 3.8$ KJ/mol

Desorption activation energy described by: $\ln T_m = E_d/RT_m$ indicates very desirable binding energy!

Iron is not a known metal hydride.  Hydrogen adsorption at near ambient conditions is also **not** anticipated on MWNTs

# Interactions and Collaborations

**Participation in IEA Annex 17 on Hydrogen Storage**

**Co-organization of Hydrogen Storage Conferences**
   Spring 2005 MRS symposium (Dillon)
   Fall 2005 MRS symposium (Heben)
   DOE/IPHE/EC/IEA workshop - June 2005 (Heben)

**Synergy with two DOE/Office of Science projects**
   CNT Membranes & Adsorbents for $CO_2$ Removal (BES/DMS)
   Linking Quantum Dots with SWNTs (BES/DCS)

**Collaborations**
Rice University (Smalley, Hauge, Yakobson), U. North Carolina (Wu, Zhou), U. Michigan (Yahgi, Yang), Caltech (Ahn, Bowman, Grubbs), Air Products (Pez, Cooper, Cheng), LLNL (Satcher, Baumann), ORNL (Geohegan, Pennycook), LBL (Zettl), NIST (Neumann), Duke (Liu), Penn State (Eklund, Foley, Crespi, Chung), U. Penn (A. MacDiarmid), SwRI (Miller, Page), BNL (Vogt, Wong), SRTC (Zidan), Stanford's GCEP Program

**Multiple Presentations (NHA, MRS, ACS) & Several Publications**

# Response to Reviewers and Tech Team

- ✓ Employ computational methods (Reviewers)
- ✓ Widen scope (Reviewers)
- ✓ Accuracy of in-house methods (Reviewers & TT)
- ✓ Employ volumetric to confirm TPD results (TT)
- ✓ Uncertainty analysis (TT)
- ✓ Estimate volumetric performance (Reviewers & TT)

Working on:
- External validation w SwRI (Reviewers & TT)
- High-throughput experimentation (Reviewers)
- Increasing capacity on SWNT from ~2.8 (observed at peer review) to 4 wt% at room T, low P

# Future Work

- Improve correspondence between volumetric and TPD data through flow-through degas (July '04)
- Use solubilized SWNTs and apply organomettalic chemistry methods for activation
- Decouple cutting/metal incorporation steps, and investigate activation without metals
- Develop and study materials for high Low-T, Low-P storage
- Externally validate uptake results at SwRI (August '04)
- Reproducible 3% uptake in-house (August '04)
- Adapt current measurement systems to, and develop new techniques for, high throughput experimentation (Sept. '04)
  - *multisample manifolds, optical and nmr spectroscopies, computational chemistry, combinatorial syntheses*
- Discover light frameworks, with a high site density per volume, with the correct energies, to achieve DOE/HFCIT storage goals